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FACSIMILE COVER SHEET

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DATE: March 4, 2002

FROM: ANNE N. CHRISTENSON

FAX NO LATER THAN: 11:15 A.M.

Direct Phone No.: (602) 916-5478

Direct Fax No: (602) 916-5678

TO:	FIRM:	FAX NO.:	BUS NO.:
ED MAZZULLO	Ofc of Hazardous Materials Standards	(202) 366-3012	(202) 366-8553

We are sending 42 pages including this cover sheet. Please telephone (602) 916-5763 if all pages are not received.

SENDER'S REMARKS:

Originals will follow via U.S. Mail.

Am

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March 4, 2002

**VIA FACSIMILE (202) 366-3012
AND U.S. MAIL**

Mr. Edward T. Mazzullo
Director
Office of Hazardous Materials Standards (DHM-10)
Research and Special Programs Administration
400 Seventh Street, S.W.
Washington, D.C. 20590

Re: Request for Classification of Packing Group for Class 8 Material,
Metam-sodium

Dear Mr. Mazzullo:

I am writing on behalf of my client Tessenderlo Kerley, Inc. ("TKI") to request a revision in the classification of a hazardous material, metam-sodium, pursuant to 49 C.F.R. § 173.136(b). Currently, metam-sodium is not specifically identified in the hazardous materials table, although it is identified in the list of Marine Pollutants. Specifically, we are requesting that RSPA classify a material containing 42% metam-sodium ("metam-sodium") as a packing group II material. This request is a follow-up to previous requests for interpretations I have made to your office regarding this particular product.

Background; Product Testing Results

As outlined in my previous correspondence with your office, TKI has performed several tests on its metam-sodium product to determine the appropriate packing group for the product. The previous correspondence, as well as some related correspondence, is attached at Exhibit A. Four additional samples of metam-sodium were tested using the testing guidelines specified in 49 C.F.R. § 173.137. The results of those tests varied considerably, ranging from noncorrosive to a corrosive, packing group II material. In an effort to resolve the conflicting results, TKI consulted Robert W. Thomassen, DVM, a veterinary pathologist with experience in product safety studies in laboratory animals including dermal irritation studies in rabbits. Dr. Thomassen also represents TKI on the Toxicology and Regulatory Committee of the Metam Sodium Task Force and has an overall familiarity with the toxicological profile of metam-sodium.

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Mr. Edward T. Mazzullo, Director
Office of Hazardous Materials Standards (DHM-10)
Research and Special Programs Administration
March 4, 2002
Page 2

Dr. Thomassen offered several possible explanations for the conflicting test results. In brief, Dr. Thomassen informed TKI that apparently inexplicable differences in dermal irritancy tests with metam-sodium could be due to one or more of the following factors including:

- (1) natural biological variability in the test animals' response, or threshold of response, to an xenobiotic (foreign chemical)¹;
- (2) disparity in dosing regimens (e.g., were all skin sites equally prepared without cuts or abrasions, was the test article applied identically from animal to animal, were the occlusive dressings applied identically from animal to animal?);
- (3) inconsistency in recognizing, describing and grading the changes produced by the test article (e.g., did the observers differ in their ability, experience and adherence to standards as they appraised, described and graded the skin lesions?); and
- (4) the possibility that samples of metam-sodium from different sources may contain one or more different residual bioreactive compounds (aside from the principal active ingredient, sodium-N-methyldithiocarbamate) that might themselves be dermal irritants.

Any or all of these factors could have contributed to TKI's inconsistent metam-sodium dermal corrosivity test results.

The California Environmental Protection Agency's Department of Pesticide Regulation recognized similar inconsistencies in the dermal irritant properties of metam-sodium in its August 20, 1999 draft Risk Characterization Document on Metam-Sodium. On page 20 under the heading "Primary dermal irritation," it states "[p]rimary dermal studies show an inexplicable range of toxicity categories with 4 Category I (corrosive, tissue damage or scarring), 1 Category II (severe irritation at 72 hr) and 2 Category IV (mild irritation at 72 hr). Because there are no apparent differences in inert ingredients, these inconsistencies may be due to differing concentrations of impurities or to unknown variabilities in laboratory practice." This draft Risk Characterization Document is attached at Exhibit B.

In addition to the four factors listed above, it should be noted that metam-sodium decomposes rapidly when diluted and introduced into an acidic environment. This phenomenon

¹ Toxicology studies are usually designed with a group size large enough to compensate for biological variability; groups consisting of only 3 animals - as prescribed in the OECD guidelines for acute dermal irritation/corrosion testing - provide no such compensation.

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Mr. Edward T. Mazzullo, Director
Office of Hazardous Materials Standards (DHM-10)
Research and Special Programs Administration
March 4, 2002
Page 3

must be considered when interpreting the results of any toxicology study with metam-sodium, including dermal irritancy studies, since the surface of rat skin is acidic with a pH of 5. Specifically, a dermal metabolism study performed with metam-sodium and rat skin illustrated that measurable quantities of methyl isothiocyanate ("MITC")² and carbon disulfide ("CS₂")³ were generated when dilute solutions of the product contacted skin.⁴ Based on such findings, it is possible that a portion of the dermal irritancy ascribed to metam-sodium may actually be due to MITC, which is generally considered a stronger toxicant than metam-sodium.⁵

In an attempt to (i) obtain a definitive answer as to the corrosive properties of its metam-sodium product by removing the variability evident in its animal testing, and (ii) develop the proper shipping description for its metam-sodium product, TKI had four samples of metam-sodium tested using the methodology described in DOT-E 10904 (Fourth Revision). The results indicated that metam-sodium was a packing group II material. As such, TKI ships metam-sodium as a packing group II material and believes all metam-sodium should be shipped as a packing group II material.

Industry Shipping Information

The various domestic manufacturers and shippers of metam-sodium ship it as either a corrosive packing group II or a corrosive packing group III material. As described above, TKI ships its metam-sodium product as a packing group II material. TKI previously provided other metam-sodium manufacturers with the testing results described above. However, these other metam-sodium manufacturers continue to ship their metam-sodium products as packing group III material. Perhaps this is, in part, because the Hazardous Materials Regulations currently provide the metam-sodium industry with an incentive to ship metam-sodium products as packing group III materials rather than as packing group II materials. Specifically, the Hazardous Materials Regulations provide that non-DOT specification cargo tanks and portable tank motor vehicles are authorized for the shipment of packing group III material. (49 C.F.R. § 173.241) The packaging requirements for packing group II materials do not authorize the use of these non-DOT specification packaging. Thus, it can be less expensive to ship metam-sodium as a packing group III material than as a packing group II material.

TKI believes it sells about one-third of the estimated 14-20 million gallons of metam-sodium products that are sold in the United States on an annual basis. Moreover, because TKI

² MITC is the principal breakdown product and primary fumigating agent of metam-sodium in soil.

³ CS₂ is a minor breakdown product of metam-sodium.

⁴ This information is based on a study published by M. Hall in 1990 - "Metam Sodium: Preliminary In-Vitro Skin Metabolism." Relevant portions of this study are attached at Exhibit C.

⁵ See L. Jowa's 1996 study - "Metam: Animal Toxicology and Human Risk Assessment." Portions of this study are attached at Exhibit D.

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Mr. Edward T. Mazzullo, Director
Office of Hazardous Materials Standards (DHM-10)
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Page 4

also toll manufactures for another metam-sodium label holder, TKI ships more than one-third of the total estimated yearly production of metam-sodium. Of the metam-sodium shipped in the United States, TKI estimates that 10-15% is shipped via rail, with the remaining 85-90% shipped via highway. Because metam-sodium is typically double and triple handled (manufacturer to terminal to distributor to end-user), any one gallon of metam-sodium is potentially shipped multiple times. Often the end-user is a farm location that receives the product in relatively small increments (*i.e.*, approximately 1,000-2,500 gallons).

Because manufacturers of metam-sodium may make product for more than one pesticide label holder, it is possible for identical material from the same storage tank to leave the manufacturing facility under different shipping descriptions reflecting different packing groups. Also, even though a manufacturer may initially ship the metam-sodium product as a packing group II material, the label holder, distributor or end-user may change the shipping descriptor to reflect a different packing group at a later date and ship the metam-sodium product as a packing group III material in order to take advantage of the more lenient (and less expensive) packaging requirements.

Incidents involving the failure of non-DOT specification packaging do occur. We know of two such incidents that have occurred since the beginning of this year. In one instance, a plastic tank being pulled on a trailer broke apart when the trailer tipped over en route spilling 700-800 gallons of metam-sodium. In the second instance, a 1500-gallon portable tank rolled over and although it did not split open, it spilled 100 gallons of metam-potassium, a product similar to metam-sodium. We do not know whether these incidents were reported to the National Response Center. Information regarding these two incidents is attached at Exhibit E.

Request for Classification Change; Cost Analysis

Given the conflicting test results and industry shipping practices for metam-sodium, TKI previously sent a written request for interpretation to the Research and Special Programs Administration ("RSPA") to obtain RSPA's guidance regarding the appropriate packing group for TKI's metam-sodium product. Subsequently, another metam-sodium manufacturer sent a similar letter to RSPA. RSPA responded to both letters. Both RSPA letters require TKI to ship metam-sodium as a packing group II material. However, the RSPA letter to the other metam-sodium manufacturer permits that manufacturer to ship metam-sodium products as packing group III material. We believe this inconsistency must be resolved. To solve this inconsistency, TKI believes RSPA must classify metam-sodium as a packing group II material to protect (i) the health and safety of any emergency response personnel or transportation personnel that may come into contact with metam-sodium and (ii) the environment, in the event of a release of metam-sodium.

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Mr. Edward T. Mazzullo, Director
Office of Hazardous Materials Standards (DHM-10)
Research and Special Programs Administration
March 4, 2002
Page 5

By shipping metam-sodium products as packing group II material, TKI has incurred some expenses. Specifically, TKI has spent approximately \$275,000 to upgrade the tanks its customers use to ship its metam-sodium product to meet the packing group II packaging specifications. Additionally, TKI sells its metam-sodium product to customers at a reduced price (by offering rebates) in an effort to help its customers recover the costs incurred by those customers to ensure their packaging complies with the packing group II packaging specifications. In total, TKI has incurred approximately \$650,000 in expenses to date.

Conclusion

On behalf of TKI, we request that RSPA classify metam-sodium as a packing group II material for the following reasons:

1. The more protective shipping requirements for packing group II material is in the best interests of protecting (i) public safety, (ii) transportation personnel that handle metam-sodium, and (iii) emergency response personnel that respond to a release of metam-sodium; and
2. The costs to the industry associated with upgrading equipment to accommodate packing group II material are comparatively small.

Your prompt attention to this request would be appreciated. Please contact me at your earliest convenience to discuss any questions or comments you may have, or if you require further information. Thank you for your consideration.

Sincerely,



Anne N. Christenson

ANC:ep
Enclosures

cc by fax: Michael Johnson
Office of Hazardous Materials Standards
Research & Special Programs Administration

1254744.6/53078.179

EXHIBIT A

LAW OFFICES
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May 28, 2001

Mr. Ed Mazzullo, Director
Office of Hazardous Materials Standards
Research and Special Programs Administration
400 Seventh Street, SW
Washington, DC 20590-0001

Re: Request for Written Interpretation

Dear Ed:

I am writing this letter on behalf of a client who ships hazardous materials. Under the following scenarios, for purposes of applicability of 49 C.F.R. parts 170 - 179, are one or both of these companies offerors of the hazardous material ("product")?

Scenario 1: Company A owns the product. Company A manufactures the product. Company A prepares the product for shipment by marking, labeling, and packaging the product. Company A prepares the shipping papers and signs the shipper's certification.

Scenario 2: Company A owns the product, it provides the raw materials to manufacture the product, and it always has title to the product. Company B manufactures the product. Company B prepares the product for shipment by marking, labeling, and packaging the product. Company A tells Company B how to prepare shipping papers. Company B prepares the shipping papers, on Company A's bill of lading, and signs the shipper's certification. Company A selects the packaging (a cargo tank) and arranges for transportation of the product.

Thank you for your assistance with this matter. Please contact me if you have any questions.

Sincerely,



Anne N. Christenson

PHX/ACHRISTE/1186142.1/53078.179

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May 28, 2001

Mr. Ed Mazzullo, Director
Office of Hazardous Materials Standards
Research and Special Programs Administration
400 Seventh Street, SW
Washington, DC 20590-0001

Re: Request for Written Interpretation

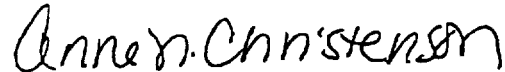
Dear Ed:

I am writing this letter on behalf of a client who ships potentially corrosive hazardous materials. My client had a product tested to determine its corrosivity and degree of danger. Four samples of the product were tested using the testing requirements specified in 49 C.F.R. § 173.137. These test results varied considerably; the results ranged from noncorrosive to a packing group II material. My client then had four samples of the product tested using the methodology in DOT-E 10904 (Fourth Revision). All these test results indicated that the product was a packing group II material. Based on these varying testing results, which packing group do the Hazardous Materials Regulations require my clients to use and why?

Thank you for your assistance with this matter. Please contact me if you have any questions.

Sincerely,

FENNEMORE CRAIG



Anne N. Christenson

PHX/ACHRISTE/1186141.1/53078.179



U.S. Department
of Transportation
**Research and
Special Programs
Administration**

400 Seventh St., S.W.
Washington, D.C. 20590

JUL 3 2001

Anne N. Christenson, Esq.
Law Office of Fennemore Craig
3003 North Central Avenue, Suite 2600
Phoenix, Arizona 85012-2913

Reference No. 01-0135

Dear Ms. Christenson:

This is in response to your May 28, 2001 letter and several telephone conversations with members of my staff concerning a product your client tested for corrosiveness using the methods prescribed in 49 CFR 173.137 and exemption DOT-E 10904. You stated the four samples tested according to § 173.137 classified the material either as non-hazardous or as Class 8 (corrosive), Packing Group II. The four samples tested according to DOT-E 10904 all classified the material as Class 8, Packing Group II. You asked which test result your client should use to classify the material.

If several tests give different results on whether a material is or is not a hazardous material, the most conservative test result should be used to establish its classification under the Hazardous Material Regulations (49 CFR Parts 171-180). For your client, based on the information you provided, this would mean classifying the material as Class 8, Packing Group II.

I hope this satisfies your request.

Sincerely,

Hattie L. Mitchell
Chief, Regulatory Review and Reinvention
Office of Hazardous Materials Standards

RECEIVED A. CHRISTENSON

JUL 09 2001

ACTION _____



U.S. Department
of Transportation
Research and
Special Programs
Administration
AUG 20 2001

400 Seventh St., S.W.
Washington, D.C. 20590

Anne N. Christenson, Esq.
Law Offices of Fennemore Craig
3003 North Central Avenue
Suite 2600
Phoenix, AZ 85012-2913

Ref. No. 01-0136

Dear Ms. Christenson:

This is in response to your letter dated May 28, 2001, requesting clarification of the term "offeror" under the Hazardous Materials Regulations (HMR; 49 CFR Parts 171-180). Specifically, you present the following two scenarios and ask whether these activities are subject to the HMR.

In the first scenario, Company A performs all offeror functions, such as selecting and preparing packages for shipment and generating shipping papers for their product. As such, Company A would be considered the offeror for purposes of HMR applicability.

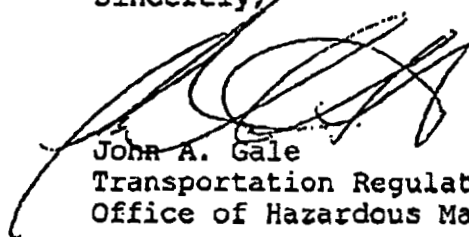
In the second scenario, Company B physically prepares packages containing Company A's product and generates shipping papers with Company A's oversight. Company A selects the packaging for their product. Because Company A and Company B split the performance of offeror functions, both companies are subject to the HMR as offerors.

The requirements of the HMR apply to persons who offer for transportation, accept for transportation or transport hazardous materials. Any one of several entities in a transportation movement could perform, singly or in combination, regulated functions (e.g., preparation of shipping papers, selection of packaging, etc.).

For purposes of administration and enforcement of the HMR, any person who performs, attempts to perform, or is obligated (by contract or otherwise) to perform any of the functions assigned by the HMR to an offeror in § 173.22 is subject to the HMR as an offeror.

I hope this satisfies your request.

Sincerely,



John A. Gale
Transportation Regulations Specialist
Office of Hazardous Materials Standards

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August 27, 2001

Mr. Ed Mazzullo, Director
Office of Hazardous Materials Standards
Research and Special Programs Administration
400 Seventh Street, S.W.
Washington, D.C. 20590-0001

Re: Request for a Written Interpretation

Dear Mr. Mazzullo:

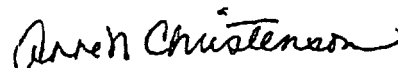
I am writing this letter on behalf of a client who ships potentially corrosive hazardous materials. This is a follow-up request based on your office's response to my May 28, 2001 letter. Thank you for your rapid response to my request. I have one further question regarding the classification of corrosive materials.

49 C.F.R. § 173.137 specifies the test methods to determine packing groups for Class 8/Corrosive material. A Department of Transportation exemption (DOT-E 10904 (Fourth Revision)) authorizes another method to determine the packing groups for a corrosive material. For the materials listed in the exemption, are both of these test methods equally valid for use in determining the classification of a hazardous material or is one more valid than the other?

Thank you for your assistance with this matter. Please contact me if you have any questions.

Sincerely,

FENNEMORE CRAIG



Anne N. Christenson

PHX/ACHRISTE/1217028.1/53078.179

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August 30, 2001

Mr. Edward H. Bonekemper, III.
Assistant Chief Counsel
Research and Special Programs Administration
400 Seventh Street, S.W.
Room 8407
Washington, D.C. 20590

Re: Request for Informal Written Interpretation

Dear Mr. Bonekemper:

I am writing on behalf of a client who ships hazardous materials. This is a follow-up request based on an earlier letter to the Office of Hazardous Materials Standards. My client would like clarification regarding whether, under the following scenario, a company has committed a "knowing" violation of the Hazardous Materials Regulations, 49 C.F.R. Parts 171-180, by its classification or description of a hazardous material.

Companies A & B ship the same product. Company A had its product and Company B's product tested for corrosivity. Those test results are conflicting (*i.e.*, the test results document that the product is either (a) consistently a Packing Group II, using the methodology specified in DOT-E 10904, or (b) nonhazardous, Packing Group III or Packing Group II, using the methodology specified in 49 C.F.R. § 173.137). Based on these test results, Company A ships the product as a Packing Group II corrosive material, as the information provided in Ms. Hattie Mitchell's July 3, 2001 letter indicates. Company A informs Company B of all these test results and the information contained in Ms. Hattie Mitchell's letter. Company B continues to ship the product as a Packing Group III material based upon test results using the methodology specified in 49 C.F.R. § 173.137. If Company B continues to ship this same product as Packing Group III, has it committed a "knowing" violation of the Hazardous Materials Regulations by misclassifying or misdescribing the material?

FENNEMORE CRAIG

Mr. Edward H. Bonekemper, III.
Page 2

Thank you for your assistance with this matter. I have attached Ms. Mitchell's July 3, 2001 letter for your convenience. Please feel free to contact me if you have any questions.

Sincerely,

FENNEMORE CRAIG

A handwritten signature in cursive script, reading "Anne N. Christenson".

Anne N. Christenson

ACHRISTE/1217132.2/53078.179



U.S. Department
of Transportation
Research and
Special Programs
Administration

400 Seventh Street, S.W.,
Washington, D.C. 20334

SEP 24 2001

Mr. Steven Charles Hunt
ShipMate, Inc.
18436 Hawthorne Blvd.
Suite 201
Torrance, CA 90504

Ref. No. 01-0231

Dear Mr. Hunt:

This is in response to your August 23, 2001 letter concerning differing test results for determining the class and packing group of 42% metam sodium solution under the Hazardous Materials Regulations (HMR; 49 CFR Parts 170 - 185). Specifically, you ask which test results performed for determining the packing group of your material should be used: the Corrositex test performed under exemption DOT-E 10904, resulting in a Packing Group II designation; or the skin necrosis test performed in accordance with § 173.137, resulting in a Packing Group III designation.

In this instance, either test by itself is sufficient to determine whether the material meets the definition of a corrosive and to determine the packing group for the material. Since use of the skin necrosis test is specified in the regulations in § 173.137, the results of that test may be used and the material may be transported as a Packing Group III corrosive material. Alternatively, the test authorized under DOT-E 10904 may be used and the material may be transported as a Packing Group II corrosive material.

I trust this satisfies your inquiry. If we can be of further assistance, please contact us.

Sincerely,



Edward T. Mazzullo
Director, Office of Hazardous
Materials Standards

EXHIBIT B

Draft

Metam Sodium (Sodium N-Methyldithiocarbamate)

RISK CHARACTERIZATION DOCUMENT



S

S

**Medical Toxicology and Worker Health & Safety Branches
Department of Pesticide Regulation
California Environmental Protection Agency**

August 20, 1999

or necrosis in the liver. Acute inhalation studies are summarized in Table 5c.

5. Local irritation

Primary eye irritation. Three of the 7 studies show these metam formulations to be Toxicity Category III eye irritants (corneal involvement or irritation for 1-7 days using 0.1 ml/eye), while the remainder show a Toxicity Category IV irritation potential (no corneal involvement, minor effects clear within 24 hr).

Primary dermal irritation. Primary dermal studies show an inexplicable range of toxicity categories, with 4 Category I (corrosive, tissue damage or scarring), 1 Category II (severe irritation at 72 hr) and 2 Category IV (mild irritation at 72 hr). Because there are no apparent differences in inert ingredients, these inconsistencies may be due to different concentrations of impurities or to unknown variabilities in laboratory practice.

Primary eye and dermal irritation studies are summarized in Table 5d.

6. Dermal sensitization

Four of the 5 dermal sensitization studies in guinea pigs gave positive responses. Metam sodium is therefore considered to be a sensitizer. Schubert, 1978, reports a similar result in humans, considering MITC to be the probable main, and metam sodium the secondary, effector. Dermal sensitization studies are summarized in Table 5e.

EXHIBIT C

C2.10/01

Mr I

ICI CENTRAL TOXICOLOGY LABORATORY
ALDERLEY PARK MACCLESFIELD
CHESHIRE UK

CATEGORY B REPORT (CONFIDENTIAL)
Not to be Copied Except by a
Reports Centre

Sponsor: Metam Sodium
Task Force c/o
J M Wagner, ICI
Americas
Sponsor Ref: MP/98/30
CTL Ref: Y06930/002
CTL Study No: XX1730
Copy No: 6

REPORT NO: CTL/L/3065

METAM SODIUM: PRELIMINARY IN-VITRO
SKIN METABOLISM


by

M Hall

THE DATA IN THIS REPORT HAVE NOT BEEN QUALITY ASSURED

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Approved for Issue: P Rose
Project Manager

Date of Issue: 29 MAR 1990

1. INTRODUCTION

Metam sodium [sodium N- methyl dithiocarbamate] is a soil sterilant. The purpose of this study was to investigate whether volatile degradation products are produced when aqueous solutions of metam sodium are applied to the surface of rat skin. This information was required in order to ensure the appropriate experimental design of a subsequent in-vivo dermal absorption study in the rat.

This study was carried out between October and November 1989. All raw data relating to this study will be retained in the Archives at ICI Central Toxicology Laboratory (CTL) for an indefinite period. Copies of this report will be held in the CTL Report Centre.

2. EXPERIMENTAL PROCEDURES

Technical grade metam sodium (CTL reference Y06930/002) was supplied as an aqueous solution containing approximately 30% test compound.

Sections of whole rat skin were prepared immediately prior to use. These were mounted in static diffusion cells which had been modified to allow the collection of headspace samples from the donor chamber. Normal saline was used as the receptor fluid.

Dilutions of the 30% solution were prepared using distilled water, to give solutions with final concentrations of 300, 30, 3 and 0.3 mg/ml. Aliquots (25ul) of these solutions were applied to the surface of the skin and spread over an area of approximately 2.5 cm². Immediately after application, the cells were assembled and suspended in a water bath at 30°C. Three cells were prepared at each application rate with an additional cell as a control. This cell contained an inert PTFE membrane in place of

skin, to which an aliquot of the 300 mg/ml solution was applied (to allow determination of any spontaneous decomposition of metam sodium under the test conditions).

Headspace samples were taken from the donor chambers 4 hours after the application and analysed for the presence of volatile components by gas chromatography/mass spectroscopy (GC/MS). Samples of headspace from the cell containing the inert membrane were also taken, the contents of the donor cell were then acidified and the headspace resampled.

The volatile components present, methyl isothiocyanate and carbon disulphide were quantified against genuine standards.

3. RESULTS AND DISCUSSION

The amounts of methyl isothiocyanate and carbon disulphide detected in the headspace, expressed as a percentage of the applied dose, are given in Table 1.

The results from the cell containing the inert membrane show that carbon disulphide is not produced unless skin is present and also that the amount of methyl isothiocyanate produced in the presence of skin is far higher than with the inert membrane.

The percentage of both compounds detected increased as the dose rate decreased. Over the range of application rates examined, the amount of methyl isothiocyanate present was always greater than that of carbon disulphide. As the proposed pathway for the decomposition of metam sodium (Figure 1) leads to the production of carbon disulphide only in the presence of acid, the finding that methyl isothiocyanate predominates, suggests that a process other than acid catalysed decomposition is involved. This might be expected since the 30% solution has a pH of approximately 10.5 and although the pH of rat skin is about 5, the resulting conditions would be basic.

From a plot of percentage decomposition product against application rate (Figure 2), it can be predicted that decomposition to produce carbon disulphide might predominate at very low concentrations.

4. CONCLUSIONS

Metam sodium is unstable when applied as an aqueous solution to rat skin, the major volatile product being methyl isothiocyanate. The process responsible is probably not simply acid catalysed decomposition but one requiring the presence of skin.

The fraction of the dose decomposed in 4 hours increases with increasing dilution due in part to an increasing contribution from acid decomposition. As the rate of decomposition is not first order (i.e. not directly proportional to the amount of metam sodium remaining) it is likely, that given viable skin, the rate would not decrease with time. This could lead to high concentrations of volatile metabolites.

Table 1. The amount (expressed as a percentage of applied dose) of methyl isothiocyanate and carbon disulphide produced after 4 hours exposure to rat skin or an inert membrane (control).

Concentration applied (% metam sodium)	Methyl isothiocyanate (% of applied dose)	Carbon disulphide (% of applied dose)
30	1.51	0.04
3	3.94	0.36
0.3	4.80	1.59
0.03	#	3.40
Control	0.14	0
Control after acidification	0.13	0.37

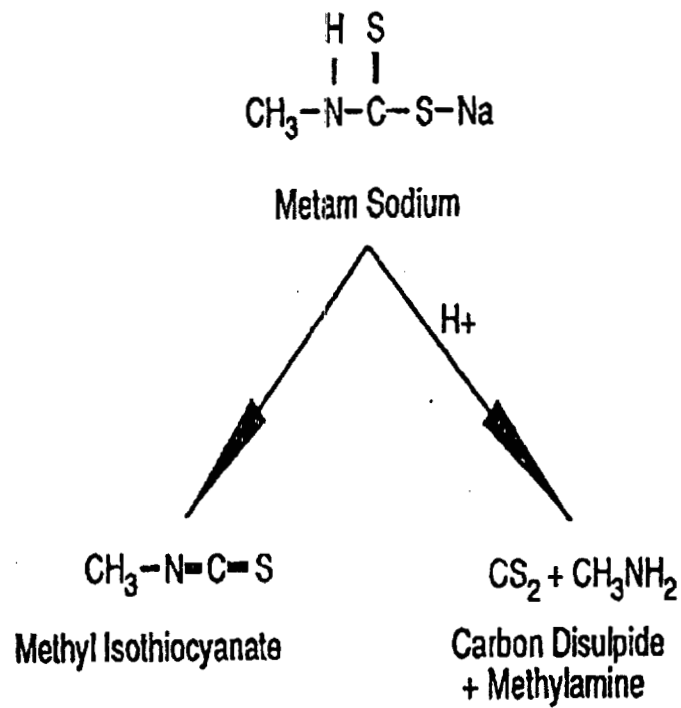
All values other than for the control are means of 3 determinations.

- Concentrations were too low for reliable quantitation.

METAM SODIUM: PRELIMINARY IN-VITRO SKIN METABOLISM

FIGURE 1

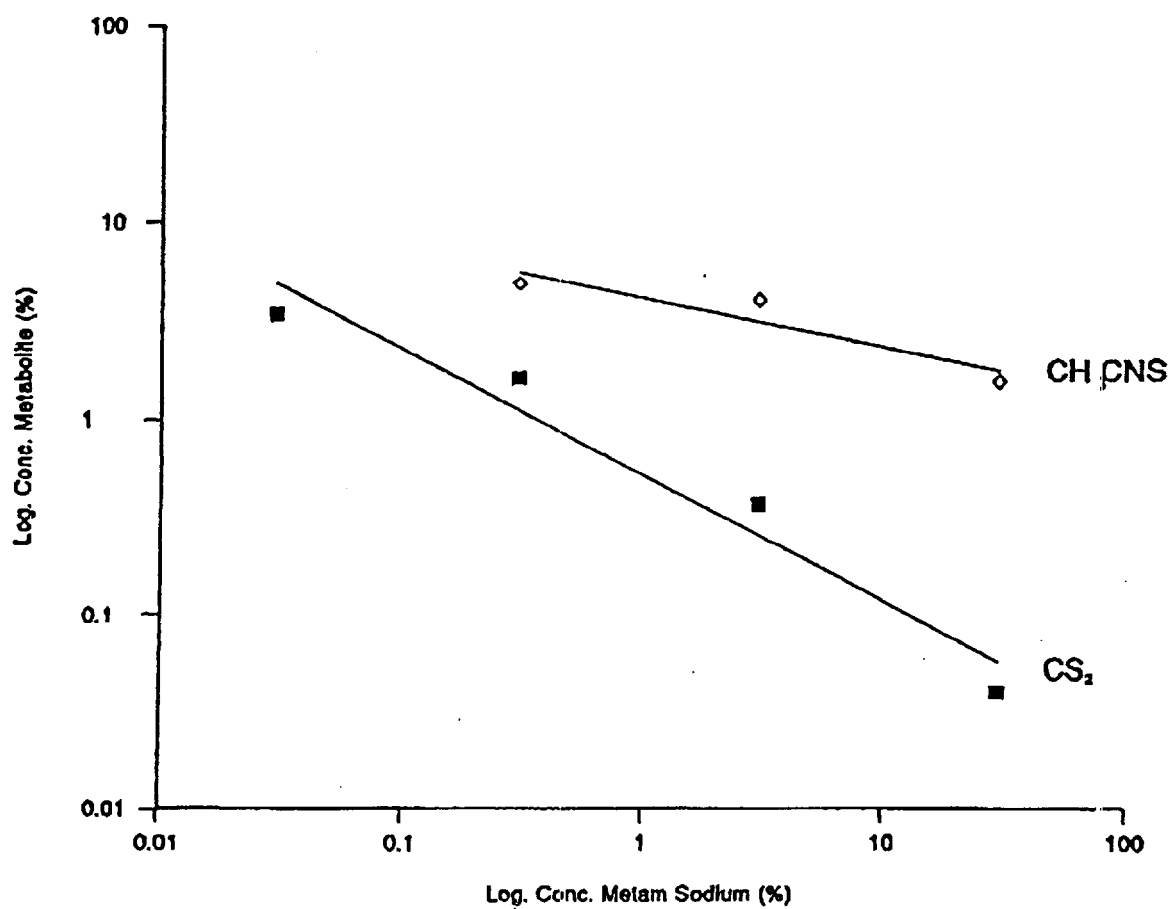
PROPOSED PATHWAY FOR THE DECOMPOSITION OF METAM SODIUM



METAM SODIUM: PRELIMINARY IN-VITRO SKIN METABOLISM

FIGURE 2

THE CONCENTRATIONS OF METHYL ISOTHIOCYANATE AND CARBON DISULPHIDE
PRODUCED AT A RANGE OF APPLICATION RATES ON SECTIONS
OF WHOLE RAT SKIN



METRAM SODIUM: PRELIMINARY IN-VITRO SKIN METABOLISM

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- 7-12. Metam sodium Task Force.

VHMPL1

EXHIBIT D

Toxicology and Risk Assessment

Principles, Methods, and
Applications

edited by

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Metam: Animal Toxicology and Human Risk Assessment

Lubow Jowa

California Environmental Protection Agency
Sacramento, California

I. INTRODUCTION

On July 14, 1991, a chemical release from a train derailment in the Upper Sacramento River resulted in the killing of fish and other aquatic wild life for miles downstream, and affected the well-being of a neighboring community (DiBartolomeis et al., 1994). The released chemical was metam (also known as metam sodium, the formulated product) used for decades throughout the world as a soil fumigant. Although not the most widely used soil fumigant, metam shows potential for broader use as other soil fumigants, such as methyl bromide or Telone, are banned or designated restricted-use materials. In addition, the potassium salt of metam is marketed as a water biocide for use in sugar processing and cooling towers; however, its use (in tonnage) is less than that of the sodium salt.

Metam is usually available as a formulation of 32.7% of the product in water, which is stable at a self-buffered pH of about 10. Once the product is diluted with additional water, as in the spill into the river, the pH decreases and metam rapidly decomposes. Resulting products consist primarily of methylisothiocyanate (MITC), H_2S , and elemental sulfur (Howd, 1992). It is the MITC, produced as the result of metam breakdown, that is considered to be the direct agent of pesticidal activity.

In the light of anticipated more extensive use of metam, it is imperative that toxicity data on this product are available, and that there is an understanding of how the data should be extrapolated to real-life situations. The present chapter represents a compilation of the health effects data on metam. For human health assessment, metam is used here as a case sample for directing attention to the evaluation of birth defects data seen in experimental animals as it relates to human exposure, and to consider the breakdown products as contributors to toxicity in humans following initial exposure to the parent compound.

whereas rodents generally received the compound in a more gradual manner by their drinking water. The bolus dose might initially produce higher blood levels of metam or its metabolites, possibly leading to hepatocyte disruption and clinical signs of liver disease. Species differences in the biotransformation of metam could also be involved, but studies comparing enzymatic or microsomal function after metam administration have not been reported. Also unknown is the potential for permanent scarring of the liver after metam-induced cell death.

It is incontrovertible that metam causes fetal loss and specific birth defects. Evidence from five studies in two species shows an increased fetal loss and potential for a rare defect, meningocele, are associated with oral intakes of metam. Therefore, metam should be considered a developmental toxicant.

There is little evidence that would indicate the mechanism of toxicity of metam, particularly how it induces death. Nesterova (1969) suggested that the effects of metam may result from a reaction with sulfhydryl groups on proteins, which then leads to disruption of cellular respiration. Although, this explanation may be adequate for the interpretation of the localized irritant effects, it does not provide an adequate explanation for the observed teratogenic or hepatotoxic effects.

The experimental results described in the foregoing indicate that metam is predominantly converted in vivo to MITC by a nonenzymatic process. The MITC is more toxic than metam in both shorter- and longer-term exposures. Besides being a strong skin irritant and sensitizer, MITC exposure produces eye and gastric irritation, significant inhibition of body weight gain, lower food consumption, decreased red cell counts and increased white cell counts, fatty changes in the liver and increases in liver weight, and decreased sperm counts (OEHHA, 1992). However, the toxicity profile of MITC does not correspond well with that of metam, except in the areas of weight loss, skin and stomach irritation and, perhaps, liver pathology.

Orally administered metam can also produce significant amounts of CS₂ in the stomach, (catalyzed by its low pH). Therefore, some of the observed toxicities seen with oral doses of metam in experimental animals (but not with MITC administration), may be mediated by the formation of CS₂. Unfortunately, the toxicity of carbon disulfide does not correspond well with metam either. Carbon disulfide is known for its neurotoxicity and cardiovascular effects reported in humans, effects that are entirely absent from the metam toxicity profile (ATSDR, 1992). However, carbon disulfide toxicity has not been studied well in experimental animals. Carbon disulfide is known to reversibly inhibit cytochrome P-450 enzymes; and thus may modulate toxicities of other metam metabolites, notably MITC (Masuda, 1986).

The differences in the toxicity profiles for metam and MITC compounds could also be due to the substantially higher experimental doses of administered metam, when compared with doses of administered MITC. The results of dermal, inhalation, and oral studies indicate that animals were more able to tolerate higher doses of metam than MITC. MITC is much more irritating and inhibiting to normal feeding behavior than metam (OEHHA, 1992). Maximum doses administered to animals were typically three times higher for metam than for MITC. It is possible that some reported effects observed with metam administration were due to MITC, as the result of higher internal doses of MITC achieved from metabolism of metam than from direct administration of MITC.

B. Human Health Implications and Risk Assessment

Metam itself is relatively nonvolatile. However, inhalation of contaminated air was the most significant source of exposure following the metam spill because of the rapid conversion in the river of metam to its volatile and more toxic breakdown product MITC. This conversion should be considered in future risk assessments. In this toxic spill, eye irritation, headache, and respiratory effects were the most common complaints in effected individuals. It was likely that

EXHIBIT E

STATE OF CALIFORNIA TRAFFIC COLLISION REPORT

CHP 555 Page 1 (Rev. 8-87) OPT042

SPECIAL CONDITIONS HAZARDOUS MATERIAL		DRIVER LICENSE <input checked="" type="checkbox"/>	DRIVER LICENSE <input type="checkbox"/>	CITY UNINC.	JUDICIAL DISTRICT N. Kern - Delano	LOGAL REPORT NUMBER 2002010255
COLLISION OCCURRED ON STATE ROUTE 43		DAY 01	MONTH 24	YEAR 02	TIME (HOUR) 1000	NOC # 9426
REPORT INFORMATION .5		DAY OF WEEK 8 M T W T F S		TOW AWAY <input checked="" type="checkbox"/> YES <input type="checkbox"/> NO		PHOTOGRAPHS BY: <input checked="" type="checkbox"/> NONE
AT INTERSECTION WITH .5		STATE HWY RAIL <input checked="" type="checkbox"/> YES <input type="checkbox"/> NO		OFFICIAL I.D. 15145		
LOCATION 1	DRIVER'S LICENSE NUMBER AS1664785	STATE CA	CLASS C	SAFETY EQUIP. 6	VEH. YEAR 2001	MAKE/MODEL/COLOR DODGE / PUP / WHITE
DRIVER <input checked="" type="checkbox"/>	NAME (FIRST, MIDDLE, LAST) GREG SOUTHWORTH			LICENSE NUMBER 6F52236	STATE CA	
STREET ADDRESS 300 COFFEE RD #119	CITY/STATE/ZIP BAKERSFIELD, CA 93309			OWNER'S NAME UNITED AGRI PRODUCTS		
SEX M	HAIR BRN	EYES BRN	HEIGHT 6-2	WEIGHT 215	BIRTHDATE 6/6/75	OWNER'S ADDRESS 307 INTERNATIONAL AVE CIRCLE 210
HOME PHONE (661) 549-1218	BUSINESS PHONE (661) 393-2190			DISPOSITION OF VEHICLE ON ORDERS OF: <input type="checkbox"/> OFFICER <input checked="" type="checkbox"/> DRIVER <input type="checkbox"/> OTHER		
INSURANCE CARRIER CONTINENTAL CASUALTY	POLICY NUMBER GARTENSHAF			PRIOR MECHANICAL DEFECTS: <input checked="" type="checkbox"/> NONE APPARENT <input type="checkbox"/> REFER TO NARRATIVE		
OR OF TRAVEL ON STREET OR HIGHWAY S	SPEED LIMIT 55	VEHICLE IDENTIFICATION NUMBER 22129		CHP USE ONLY VEHICLE TYPE UNK <input type="checkbox"/> NONE <input type="checkbox"/> MINOR <input checked="" type="checkbox"/> MOD. <input type="checkbox"/> MAJOR <input type="checkbox"/> ROLL-OVER		
PARTY 2	DRIVER'S LICENSE NUMBER	STATE	CLASS	SAFETY EQUIP.	VEH. YEAR	MAKE/MODEL/COLOR
DRIVER	NAME (FIRST, MIDDLE, LAST)			LICENSE NUMBER	STATE	
STREET ADDRESS	CITY/STATE/ZIP			OWNER'S NAME		
SEX	HAIR	EYES	HEIGHT	WEIGHT	BIRTHDATE	OWNER'S ADDRESS
HOME PHONE	BUSINESS PHONE			DISPOSITION OF VEHICLE ON ORDERS OF:		
INSURANCE CARRIER	POLICY NUMBER			PRIOR MECHANICAL DEFECTS:		
OR OF TRAVEL ON STREET OR HIGHWAY	SPEED LIMIT	VEHICLE IDENTIFICATION NUMBER		CHP USE ONLY		
PARTY 3	DRIVER'S LICENSE NUMBER	STATE	CLASS	SAFETY EQUIP.	VEH. YEAR	MAKE/MODEL/COLOR
DRIVER	NAME (FIRST, MIDDLE, LAST)			LICENSE NUMBER	STATE	
STREET ADDRESS	CITY/STATE/ZIP			OWNER'S NAME		
SEX	HAIR	EYES	HEIGHT	WEIGHT	BIRTHDATE	OWNER'S ADDRESS
HOME PHONE	BUSINESS PHONE			DISPOSITION OF VEHICLE ON ORDERS OF:		
INSURANCE CARRIER	POLICY NUMBER			PRIOR MECHANICAL DEFECTS:		
OR OF TRAVEL ON STREET OR HIGHWAY	SPEED LIMIT	VEHICLE IDENTIFICATION NUMBER		CHP USE ONLY		
PREPARED BY M. CHOATE #15145	DISPATCH NOTIFIED <input type="checkbox"/> YES <input type="checkbox"/> NO <input checked="" type="checkbox"/> N/A	DATE 02/20/02	TIME 11:42	OFFICER Coroner	PRODUCED Produced	DATE REVIEWED 1:30:02

02/20/2002 09:00

8053948607

STATE OF CALIFORNIA TRAFFIC COLLISION CODING JHP 558 Page 2 (Rev. 8-87) OF 1042

DATE OF COLLISION (MO. DAY YEAR) 01 24 02 TIME (HOUR) 1000

OFFICER NO. 15745

PROPERTY DAMAGE

SEATING POSITION

OCCUPANTS

SAFETY EQUIPMENT

EJECTED FROM VEHICLE

ITEMS MARKED BELOW FOLLOWED BY AN ASTERISK (*) SHOULD BE EXPLAINED IN THE NARRATIVE

PRIMARY COLLISION FACTOR

TRAFFIC CONTROL DEVICES

TYPE OF VEHICLE

WEATHER (MARK 1 TO 2 ITEMS)

LIGHTING

ROADWAY SURFACE

ROADWAY CONDITION(S)

PEDESTRIAN ACTIONS

OTHER ASSOCIATED FACTOR(S)

SECURITY - DRUG / PHYSICAL

SPECIAL INFORMATION

MISCELLANEOUS

SKETCH

DATE OF COLLISION (MO. DAY YEAR)

TIME (HOUR)

OFFICER NO.

PROPERTY DAMAGE

SEATING POSITION

OCCUPANTS

SAFETY EQUIPMENT

EJECTED FROM VEHICLE

ITEMS MARKED BELOW FOLLOWED BY AN ASTERISK (*) SHOULD BE EXPLAINED IN THE NARRATIVE

PRIMARY COLLISION FACTOR

TRAFFIC CONTROL DEVICES

TYPE OF VEHICLE

WEATHER (MARK 1 TO 2 ITEMS)

LIGHTING

ROADWAY SURFACE

ROADWAY CONDITION(S)

PEDESTRIAN ACTIONS

OTHER ASSOCIATED FACTOR(S)

SECURITY - DRUG / PHYSICAL

SPECIAL INFORMATION

MISCELLANEOUS

SKETCH

STATE OF CALIFORNIA
NARRATIVE/SUPPLEMENTAL
 CHP 558

PAGE 3

DATE OF INCIDENT	TIME (2400)	NCIC NUMBER	OFFICER I.D. NUMBER	NUMBER
01-24-02	1000	9420	15145	-

NOTIFICATION:

I received a call of a collision with no details at 1010 hours. I responded from Bakersfield Area CHP office and arrived at the scene at 1028 hours.

All times, speeds and measurements in this report are approximate. Measurements were obtained by odometer and estimation.

HAZARDOUS MATERIALS:

The hazardous material spilled in this incident was Sodium N-Methyl Dithiocarbamate pesticide, with ID #2772. There was approximately 700-800 gallons of the liquid that spilled onto the dirt shoulder. The clean up and disposal was handled by Advance Clean Up Technologies out of Bakersfield. They dug up and removed all the contaminated soil and transported it to an approved disposal site. The tank trailer was not required to have a placard due to it being an implement of husbandary. There was no danger to life or health to the involved personnel at the scene.

STATEMENTS:

Party #1 (P-1, Southworth) was contacted at the command post that was set up at Sherwood Ave. P-1 related in essence that he was driving s/b at 20-25 miles per hour pulling the tank trailer. He noticed a truck coming up behind him so he moved over toward the white line to allow the truck to see around him. That's when his trailer started weaving and then it tipped over.

SUMMARY:

P-1 was driving s/b on SR-43 at 20-25 miles per hour and pulling a 2 axle tank trailer containing the aforementioned hazardous material. P-1 steered to the right toward the shoulder on the west side of the roadway to allow faster moving vehicles to see around him. This steering movement caused the liquid in the tank to splash, which made the trailer become unstable. P-1 was unable to regain control of the trailer and it tipped over onto its side spilling its contents onto the west shoulder of SR-43.

AREA OF IMPACT: (AOI)

AOI #1 (V-1's trailer rollover) was determined to be .5 of a mile n/of the n/ prolongation line of Sherwood Ave. and 4' w/of the w/ roadway edge of SR-43.

CAUSE:

P-1 caused this collision by driving in violation of section 22107 vc, unsafe turning movement. The unsafe turning movement was P-1 steering back to the left which caused the trailer to flip onto its right side.

The AOI and cause were established by statements, physical evidence and vehicle damage.

PREPARER'S NAME	I.D. NUMBER	DATE	REVIEWER'S NAME	DATE
M. Choate	15145	01-26-02		

STATE OF CALIFORNIA
NARRATIVE/SUPPLEMENTAL
CHP 568

PAGE 4

DATE OF INCIDENT	TIME (2400)	NCIC NUMBER	OFFICER I.D. NUMBER	NUMBER
01-24-02	1000	9420	15145	

- 1
- 2 RECOMMENDATIONS:
- 3 None

PREPARER'S NAME	I.D. NUMBER	DATE	REVIEWER'S NAME	DATE
M. Choate	15145	01-26-02		

02/20/2002 16:07 FAX 916 448 3850
02/20/2002 15:55 6613917839

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KERN COUNTY ARSON

@002:
PAGE 02

Printed: 02/20/2002 15:15:47

Kern County
Page: 1

Incident Report
2002-0205913-000

Basic	
Alarm Date and Time	10:25:31 Wednesday, February 6, 2002
Arrival Time	10:38:17
Controlled Date and Time	
Last Unit Cleared Date and Time	13:34:07 Wednesday, February 6, 2002
Response Time	0:12:46
Priority Response	Yes
Completed	Yes
Release to Public	Yes
Fire Department Station	ODF
Shift	A
Incident Type	422 - Chemical spill or leak
Aid Given or Received	1 - Mutual aid received
Mutual Aid Department	KCBH
Alarms	1
Action Taken 1	43 - Hazardous materials spill control and confinement
Apparatus - Suppression	3
Personnel - Suppression Personnel	8
Property Loss	\$0.00
Contents Loss	\$0.00
Property Value	\$0.00
Contents Value	\$0.00
Hazardous Material Released	0 - Special hazmat actions required or spill greater than 55 gallons
Property Use	961 - Highway or divided highway
Location Type	Intersection
Address	On hwy 58 at Tracy AV
City, State Zip	Buttonwillow, CA 93206
District	010
Census Tract	010

Hazmat	
Outside of Structure	1
Area Affected	1 - Square Feet
Area Affected Units	20
Hazmat Action Taken 1	13 - Hazmat spill control and confinement
Cause of Release	3 - Container or containment failure
Factors Contributing To Release 1	50 - Mechanical failure, malfunction, other
Mitigating Factors 1	00 - Other factor affected mitigation
Disposition	4 - Released to county agency
DOT Hazard Classification	3266
Equipment Type	881 - Model vehicles.
Equipment Model	trailer

Hazmat Chemicals	
Chemical Name	Hazardous Material
DOT ID	61 - Division 6.1 Toxic materials
Container Type	10 - Portable container, other
Estimated Container Capacity	1500
Estimated Amount Released	100
Released Units	12 - Gallons

02/20/2002 18:07 FAX 916 448 3850
02/20/2002 15:55 6613917039

KSC LLP SAC
KERN COUNTY ARSON

0003
PAGE 03

Kern County
Page: 2

Incident Report
2002-0205913-000

Printed: 02/20/2002 15:55:47

Hazard Chemicals	
Physical State When Released	2 - Liquid
Released Into	3 - Ground
Apparatus - E25	
Apparatus ID	E25
Response Time	0:12:46
Apparatus Dispatch Date and Time	10:25:31 Wednesday, February 6, 2002
En route to scene date and time	10:25:31 Wednesday, February 6, 2002
Apparatus Arrival Date and Time	10:38:17 Wednesday, February 6, 2002
Apparatus Clear Date and Time	13:34:07 Wednesday, February 6, 2002
Apparatus priority response	Yes
Number of People	3
Apparatus Use	1
Apparatus Action Taken 1	43 - Hazardous materials spill control and confinement
Apparatus Type	11 - Engine
Personnel 1	K0172 - Martinez, Joel J Position: 4589 C
Personnel 2	K0700 - Moore, Justin Position: 4640
Personnel 3	K0281 - Houck, James E Position: 4594 C
Personnel Action Taken 1: 43 - Hazardous materials spill control and confinement	
Apparatus - E66	
Apparatus ID	E66
Response Time	1:02:46
Apparatus Dispatch Date and Time	10:28:31 Wednesday, February 6, 2002
En route to scene date and time	10:29:31 Wednesday, February 6, 2002
Apparatus Arrival Date and Time	11:32:17 Wednesday, February 6, 2002
Apparatus Clear Date and Time	13:13:07 Wednesday, February 6, 2002
Apparatus priority response	Yes
Number of People	3
Apparatus Use	1
Apparatus Action Taken 1	43 - Hazardous materials spill control and confinement
Apparatus Type	11 - Engine
Personnel 1	K0611 - Blue, James N Position: 4639
Personnel 2	K0156 - Eppley, Steven C Position: 4589 C
Personnel 3	K0618 - Pendergrass, Steven Position: 4639
Apparatus - HM66	
Apparatus ID	HM66
Response Time	1:02:46
Apparatus Dispatch Date and Time	10:28:31 Wednesday, February 6, 2002
En route to scene date and time	10:29:31 Wednesday, February 6, 2002
Apparatus Arrival Date and Time	11:32:17 Wednesday, February 6, 2002
Apparatus Clear Date and Time	13:13:07 Wednesday, February 6, 2002

Supra, Inc. FireRMS 5.0 Version: 1.26.43



02/20/2002 16:07 FAX 816 448 3850
02/20/2002 15:55 6613917039

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KERN COUNTY ARSON

0004
PAGE 04

Printed: 02/20/2002 15:05:47

Kern County
Page: 3

Incident Report
2002-0205913-000

Apparatus - EM66	
Apparatus priority response	Yes
Number of People	2
Apparatus Use	1
Apparatus Action Taken 1	43 - Hazardous materials spill control and confinement
Apparatus Type	93 - HazMat unit
Personnel 1	K0271 - Putnam, Kenneth Position: 4594 C
Personnel 2	K0671 - Tucker, Duane K Position: 4639

Authority	
Reported By	K0172 - Martinez, Joel J 15:56:52 Wednesday, February 6, 2002
Officer In Charge	-
Reviewer	-

Narratives	
Narrative Name	CAD Narrative
Narrative Type	CAD Narrative
Author	-
Narrative Text	0205913 HM1 HAZMAT LEVEL 1 Incident
Narrative Name	e25
Narrative Type	Incident
Narrative Date	15:53:09 Wednesday, February 6, 2002
Author	K0172 - Martinez, Joel J
Author Rank	4589 C
Author Assignment	1
Narrative Text	100 gal. of K Para released on ground next to hwy 58. chp on scene company 25 requested haz mat 66, area was confined kern co. enviro. health took charge of scene

End of Report





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Local news

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Toxic spill clogs traffic on 58

The Bakersfield Californian

Wednesday February 06, 2002, 10:40:23 PM

Highway 58 was closed in both directions for more than four hours Wednesday after 500 gallons of pesticide spilled from an overturned trailer under the Interstate 5 overcrossing in Buttonwillow.

The driver of a pickup hauling a 1,500-gallon plastic tank containing soil fumigant tried entering the dirt shoulder off westbound Highway 58, said Kern County Fire Capt. Tomas Patlan.

The motion caused the pesticide to slosh inside the tank and tip the trailer over near a railroad siding, Patlan said. Highway 58 at the I-5 overpass was cleared and traffic was allowed to pass by 2:57 p.m., the California Highway Patrol reported.

No one was injured during the 10:30 a.m. accident but 12 Kern County firefighters and a state hazardous materials team went to the site, Patlan said.

The driver, a farm worker whose name was not available, was heading for a farm property when he left Highway 58, Patlan said.

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February 27, 2002

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Local Poll - Previous Results

FG&E rescued a cat from a power pole after it was stuck there for more than six days. What is the best way to get a cat off a pole?

- ☐ Set out some food and leave the cat ALONE. The neighbors were probably scaring it to death.
- ☐ Call The Californian and let the paper make a big deal out of it.
- ☐ Cat on a pole? Problem?
- ☐ Utility workers or the Fire Department should have been

